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INFLUENCE OF THE TYPE OF RARE-EARTH CATION ON ELECTRICAL PROPERTIES OF BA(ZR,TI)O_3 CERAMICS

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● Resumen

En este artículo es investigado el efecto del radio iónico de diferentes cationes de tierras raras sobre las propiedades eléctricas del compuesto Ba(Zr,Ti)O_3. La cerámica $BaZr_{0.09}Ti_{0.9}O_3$ fue dopada con iones de Gd^{3+}, Pr^{3+} y La^{3+}, sustituyendo un 5 % de contenido de cationes Ba^{2+}. Los resultados muestran que el coeficiente de difusividad se incrementa con el aumento del radio iónico, mientras el carácter de la transición de fase permanece casi constante, de acuerdo con el modelo fenomenológico de Santos-Eiras. En todas las muestras se reporta un comportamiento no relajador. El proceso de conductividad iónica en el $BaZr_{0.09}Ti_{0.9}O_3$ aparece a 200 ºC, valor inferior al observado en el material cerámico $BaTiO_3$. El valor de energía de activación en el proceso de conductividad del $BaZr_{0.09}Ti_{0.9}O_3$ (E_a= 0.81 eV) indica un mecanismo de compensación de carga en la estructura cristalina similar al $BaTiO_3$, es decir vacancias de oxígeno simplemente ionizadas. Para el compuesto $BaZr_{0.09}Ti_{0.9}O_3$ dopado con iones Gd^{3+}, Pr^{3+} y La^{3+} aparece además un mecanismo de conducción de electrones, debido a la sustitución del Ba^{2+}.

Palabras clave: material con base de $BaTiO_3$, cerámica $BaZrTiO_3$, estructura de defectos, proceso de conductividad, propiedades dieléctricas.

● Abstract

In this paper the effect of the ionic radius of different rare-earth cations on the electrical properties of the Ba(Zr,Ti)O_3 (BZT) compound is investigated. Ln-doped $BaZr_{0.09}Ti_{0.9}O_3$ samples (Ln = Gd^{3+}, Pr^{3+} and La^{3+} ions), with a 5 % of Ba^{2+} cation substitution, are obtained by conventional ceramic method. The effect of rare-earths addition on phase transition and conductivity process of BZT is analyzed. Results show diffusivity coefficient increases with increasing ionic radius of lanthanide cation, while the character of the phase transition remains constant, according to the Santos-Eiras phenomenological model. The all studied samples showed non relaxor behaviour. The ionic conductivity process appears at 200 ºC in BZT ceramic, being lower than the value bserved in $BaTiO_3$ material. The value of activation energy in BZT ceramic (E_a= 0.81 eV) indicates a charge compensation mechanism in the crystalline structure similar to the $BaTiO_3$ material, i.e. singly ionised oxygen vacancies. A compensation mechanism for conduction electrons, due to the substitution of Ba^{2+}, is added for Gd^{3+}-, Pr^{3+}- and La^{3+}- doped $BaZrTiO_3$ compounds.

Keywords: Ba(Zr,Ti)O_3 ceramics, defects structure, lanthanides doped BZT, conductivity process, dielectric properties.

● Introduction

Rapid development of wireless communications requires tunable microwave devices with typical functional components /1-3/. The ferroelectric $BaTiO_3$-based exhibit a high non-linearity and are the systems with higher capacities for these applications: tunable ceramics, capacitors and microwave devices /4, 5/. Materials with high tunability, low dielectric loss and moderate dielectric constants are desirable for tunable microwave applications /3/.

The $BaZr_xTi_{1-x}O_3$ (BZT) system, a leading member of the $BaTiO_3$ (BT) based family, has received great attention in the last decade due to its dielectric response features. These ceramics have a high voltage-resistance characteristic because Zr^{4+} is chemically more stable than Ti^{4+}. In addition, BZT systems exhibit better thermal stability than the $Ba_{1-x}Sr_xTiO_3$ (BST) systems /6, 7/ in the paraelectric region.

Properties of BZT are highly dependent on the amount of Zr^{4+} cation /8, 9/. The system exhibits a phase transition that changes its character according to the concentration of Zr^{4+}. Thus, a ferroelectric behaviour with a "normal" or "classic" phase transition is displayed for $0 < x < 0,10$ while a relaxor behaviour, where the temperature corresponding to maximum dielectric constant (Tm) depends on the frequency of electric field, is detected for $0,25 < x < 0,75$. A polar cluster like behaviour is obtained for Zr-rich BZT compositions. These limits may move according to the method of preparation, the presence of secondary phases and microstructural features such as porosity, grain size, etc. /8-11/.

Ciomaga *et al*. /12/ found relaxor properties with diffuseness of phase transition in the study of the dielectric response of the $Ba(Zr_xTi_{1-x})O_3$ ceramic system with x = 0,10; 0,15 and 0,18. The maximum temperature was shifted from 2 to 5 ºC in the frequency range from 1 to 10^5 Hz for T > 100 ºC. The diffusivity coefficient, δ, increased sharply for high-Zr and this fact was interpreted as a consequence of the contribution of thermally activated space charge by local compositional and electrical heterogeneities /10, 11/.

Recently, several authors have reported the improvement of the ferroelectric properties of $BaTiO_3$-based ceramics by doping with rare-earth ions /13, 14/. Chou *et al*. /14/ studied $Ba_{1-x}Ln_xZr_{0.2}Ti_{0.8-x/4}O_3$ system for Ln = La, Sm, Eu, Dy and Y, where they introduce various rare-earth cations with different ionic radius.

The research draws attention about the effect of ionic radii of the rare-earth cation on the dielectric properties and its relaxor behaviour. A peak broadening of the phase transition, called diffuse phase transition (DPT), and a non-Curie-Weiss behaviour (non-classic ferroelectric behaviour) for rare-earth doped BZT compounds were reported by these authors /14/.

The aim of this paper is to investigate phase transition characteristics and the conductive process in $(Ba_{1-y}Ln_{3y/2})(Zr_{0.09}Ti_{0.91})O_3$ system. In order to study the influence of the type of rare-earth cation on electrical properties of this system, dodecahedral Ba^{2+} sites were partially substituted by La^{3+}, Gd^{3+} or Pr^{3+} ions.

Experimental procedure

Compounds with the general formula $(Ba_{0.95}Ln_{0.033})Zr_{0.09}Ti_{0.91}O_3$ for Ln = Gd^{3+}, Pr^{3+} and La^{3+} have been synthesized. A 9 % zirconium concentration has been chosen, since Ln-free compound (y = 0,00) does not show relaxor behaviour /15/. Ceramics were obtained by using a modification of the solid state reaction method /16/ from TiO_2 (Probus 99,9 %), $BaCO_3$ (Probus 99 %), ZrO_2 (Fluka 99 %), Pr_6O_{11} (Aldrich 99,9 %), Gd_2O_3 (Aldrich 99,9 %) and La_2O_3 (Aldrich 99,98 %) raw materials.

Oxides were treated at 900 ºC for 8 hours before the weighing process. The mixture was homogenised in acetone by magnetic stirring for 2 hours. Once the solvent had evaporated, pellets of ~1 g were obtained by applying 100 MPa of uniaxial pressure. Pellets were thermally treated at 1 250 ºC for 10 hours.

After grinding, pellets were sintered at 1 500 ºC for 8 hours under air atmosphere. Sintering process was divided in two steps (5h + 3h) with an intermediate grinding process in order to obtain a better density. The cooling rate was 2 ºC min^{-1}. In table I is related denomination and stoichiometry of the samples.

TABLE 1. STOICHIOMETRIC AND DENOMINATION FORMULA OF THE SAMPLES

Denomination	Stoichiometric formula
BZT	$BaZr_{0.09}Ti_{0.91}O_3$
BGZT	$(Ba_{0.95}Gd0_{.033})Zr_{0.09}Ti_{0.91}O_3$
BLZT	$(Ba_{0.95}La_{0.033})Zr_{0.09}Ti_{0.91}O_3$
BPZT	$(Ba_{0.95}Pr_{0.033})Zr_{0.09}Ti_{0.91}O_3$

Lattice parameters of the ceramics were determined by the x-ray powder diffraction technique using a PANalytical X'Pert PRO MPD system with Cu kα radiation and an X´Celerator detector equipped with a focusing primary Ge(111) monochromator. Diffraction patterns were collected in Bragg-Brentano geometry for 2θ from 4° to 80° at room temperature. The data were analysed by the Rietveld method using the FullProf program. Morphological study was performed by scanning electronic microscopy (SEM) with a JEOL JSM-840 instrument. Samples of diameter ~10 mm and thickness ~1 mm were covered with gold by sputtering for characterizing the dielectric properties. Dielectric response was obtained by using an Agilent E4980A Precision LCR Meter sweeping between 100 Hz and 1 000 kHz.

● Results and discussion

Figure 1 shows (a) XRD patterns obtained for the $(Ba_{0.95}Ln_{0.033})Zr_{0.09}Ti_{0.91}O_3$ system for Ln = La, Pr, and Gd and (b) an zoom for two different 2θ ranges. XRD patterns of La-, Pr- and Gd-doped BZT ceramics are single phase and isostructural with $BaTiO_3$ perovskite-type structure. A clear splitting of the tetragonal (200) and (301) reflections is observed in the Gd-doped BZT sample. Nevertheless, the Gd-doped BZT compound exhibits lattice parameters that are related to a tetragonal unit cell. This crystallographic behaviour is more evident in Gd-doped than Ln-free BZT compound, but unlike the last one, the *a* and *c* parameters switch when the system is Gd-doped.

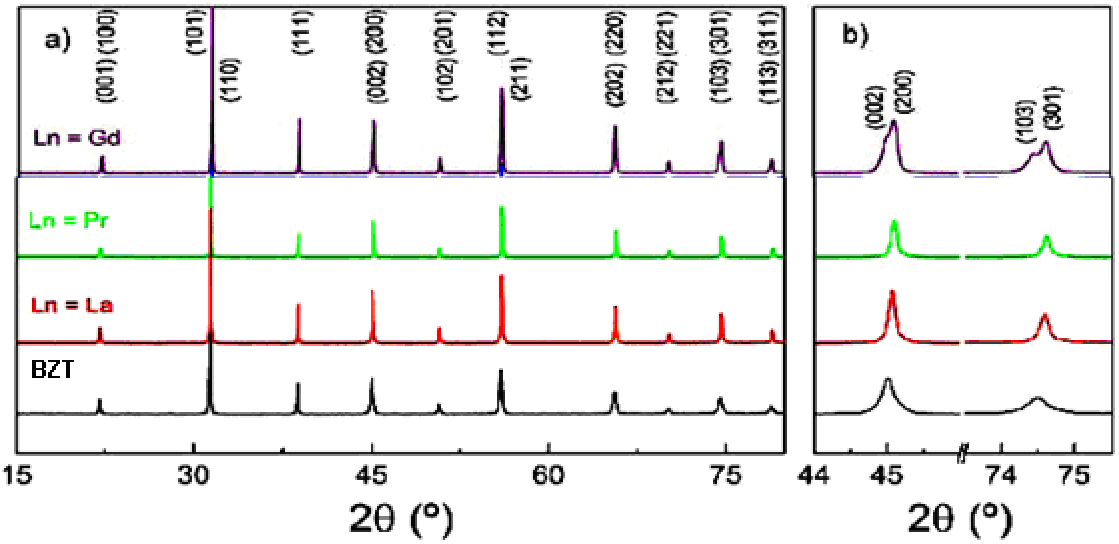

Fig. 1 Experimental XRD patterns obtained for $(Ba_{0.95}Ln_{0.033})(Zr_{0.09}Ti_{0.91})O_3$ system at room temperature (a) $15 \leq 2\theta \leq 80$; (b) reflections in the $44 \leq 2\theta \leq 50$ and $73 \leq 2\theta \leq 76$ range.

Table I shows the crystalline lattice parameters, the unit cell volume and adjustment factors obtained by Rietveld method. BZT sample has a tetragonal unit cell with ratio c/a = 1,005. This value is similar to the BT ratio, taking into account the experimental error (table II). When Ba^{2+} is substituted by Gd^{3+} onto BZT crystalline structure, the parameter ***a*** increases and ***c*** decreases with respect to the unit cell of the BZT compound.

The ratio c/a = 0,998 indicate a decreasing of the tetragonality of crystalline structure. Similar ***a*** and ***c*** lattice parameters values are obtained for La- and Pr-doped BZT compounds at room temperature. The ratio c/a = 0,999 and 1,000 1 suggest both samples are in the paraelectric cubic phase at room temperature, as can be verified in figure 4.

TABLE 2. LATTICE PARAMETERS, UNIT CELL VOLUME AND AGREEMENT FACTORS OBTAINED BY RIETVELD METHOD FOR THE $(BA_{1-Y}LN_{2Y/3})ZR_{0.09}TI_{0.91}O_3$ CERAMIC SYSTEM

$(Ba_{1-y}Ln_{2y/3})Zr_{0.09}Ti_{0.91}O_3$		Lattice parameters and unit cell volume			Agreement factors			
y	Ln	a(A)	c(A)	V(A^3)	Rp	R_{WP}	R_f	χ^2
0,00		4,022 8(1)	4,025 1(2)	65,140(4)	18,6	20,4	13,8	2,206
0,05	Gd	4,024 90(5)	4,017 42(6)	65,082(1)	20,2	18,9	12,6	2,241
0,05	La	4,020 19(6)	4,020 11(5)	64,973(2)	18,7	19,5	15,0	1,684
0,05	Pr	4,019 8(1)	4,020 5(2)	64,966(4)	26,0	34,2	18,8	3,299

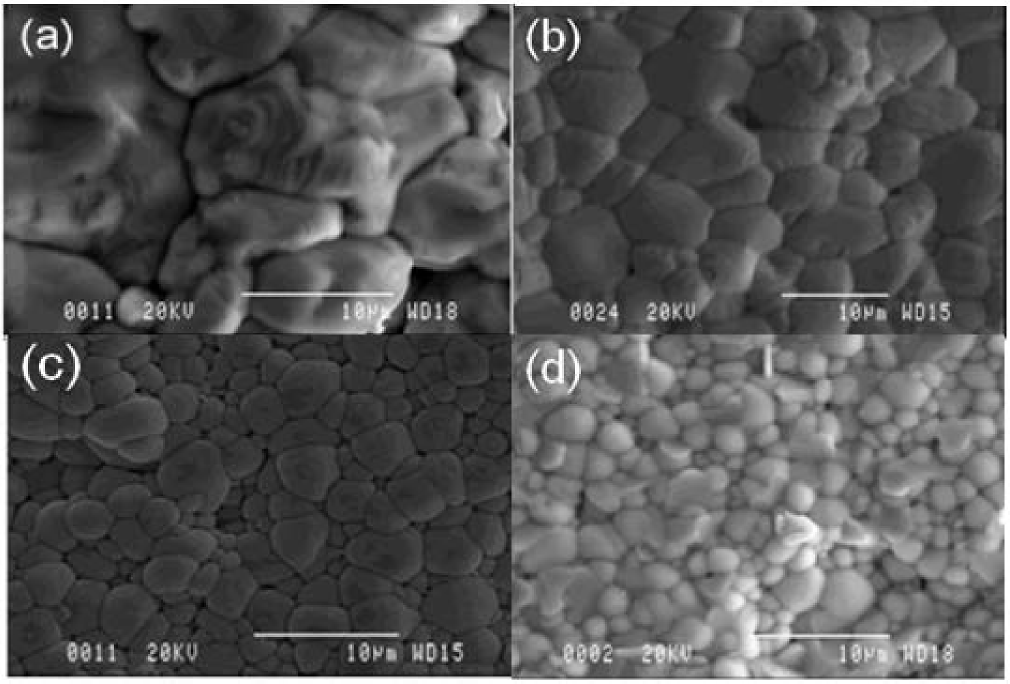

Fig. 2 SEM images of the $(Ba_{0.95}Ln_{0.33})Zr_{0.09}Ti_{0.91}O_3$ ceramic system: (a) Ln-free; (b) Ln = La^{3+}; (c) Ln = Gd^{3+}; and (d) Ln = Pr^{3+}.

Figure 2 shows SEM micrographs of the $(Ba_{1-y}Ln_{2y/3})Zr_{0.09}Ti_{0.91}O_3$ ceramic system with y = 0,05 and Ln = La, Gd, y Pr. Images show high density samples. Grain size decreases when the Ba^{2+} is replaced by rare-earth ions. This result indicates that the incorporation of La^{3+}, Gd^{3+} and Pr^{3+} onto BZT structure inhibits the grain growth.

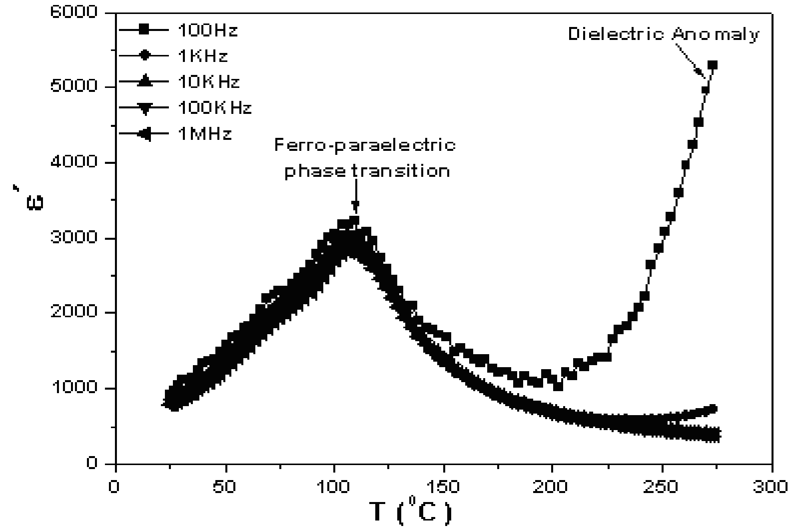

Fig. 3 Temperature dependence of the ε´ at different frequencies for Ln-free BZT ceramic.

The temperature dependence of the real part of the dielectric permittivity, ε´, at different frequencies is shown in figure 3 for Ln-free BZT ceramic. Two different behaviours are observed: (1) the ferroelectric-paraelectric phase transition (Tm ~ 110 °C) and (2) a dielectric anomaly which begins at 200 °C.

The phase transition temperature for BZT compound is less than the corresponding BT ceramics. This is due to that the Zr^{4+} ions replace Ti^{4+} cations in site B and the ionic radii of Zr^{4+} ($r_{Zr}{}^{4+}$ = 0,72 A) is greater than the radii of Ti^{4+} ($r_{Ti}{}^{4+}$ = 0,605 A), therefore Zr^{4+} cation have a lower displacement inside of the oxygen octahedron.

On the other hand, the dielectric anomaly has strong dependence with the frequency, which is more pronounced at low frequencies. In the literature this anomaly is known as low frequencies dispersion (LFD) and has been reported and investigated by several authors in the $BaTiO_3$ compound /17-20/.

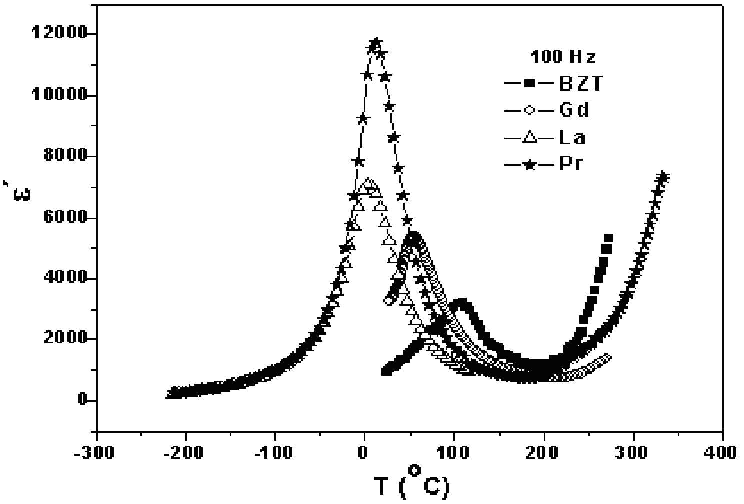

Fig. 4 Temperature dependence of the real part of the permittivity, ε´, for Ln-free and Gd-, La- and Pr-doped BZT ceramics at 100 Hz.

Figure 4 shows the temperature dependence of the ε´ for $Ba_{0.95}Ln_{0.33}Zr_{0.09}Ti_{0.91}O_3$ ceramic system for Ln = Gd^{3+}, La^{3+} and Pr^{3+} at 100 Hz. The ferroelectric-paraelectric phase transition temperature decreases with the increase of the ionic radii of the rare-earth ions substituted in the BZT ceramic. This result is in corresponding with the reported from X-ray analysis, confirming the hypothesis about the effects of the dopants in the BZT system.

The substitution of Ba^{2+} by Ln^{3+} causes a reduction of the tetragonal unit cell, and this effect increases with increasing of the ionic radii of lanthanide ion. This reduction leads to a small shift of the tetravalent cation, Ti^{4+} or Zr^{4+}, outside the center of the oxygen octahedron, and a corresponding decrease of maximum temperature /14/. The dielectric anomaly, typical of a LFD process, appears again at temperatures higher than 200 °C.

To characterize the phase transition for Ln-doped and Ln-free BZT system was used the Santos-Eiras model /21/, according to the following equation:

$$\varepsilon' = \frac{\varepsilon'_m}{1+\left(\frac{T-T_m}{\Delta}\right)^{\xi}} \qquad (1)$$

The adjustment values obtained from equation (1) are reported in Table III for ε´ vs T curve at 1 MHz. Values of the parameters Δ and ξ indicate diffuse-type phase transition and non-relaxor behaviour for Ln-free BZT ceramic. Some authors have reported normal ferroelectric phase transition, as in BT, for Zr^{4+} cation concentrations $0 \leq x \leq 0{,}1$ /4, 10, 11/.

They explain this result taking into account that in Ti-rich compositions of BZT system the octahedral site remains as ferro-active preserving the large order spontaneous polarization. As a consequence a classical ferroelectric behaviour is archived /14/. However, in this paper we report a small diffusivity in the phase transition for Zr^{4+} ions concentration x = 0,09. The diffuse nature of the phase transition might be associated with the influence of either LFD or an increase in the density of grain boundaries by decreasing its size.

On the other hand, the change of Ba^{2+} by Ln^{3+} brings the formation of point defects due to the charge compensation mechanisms in the crystalline structure. Hence, non-stoichiometric compositions are obtained $(Ba_{1"y}Ln_{2y/3}V_{y/3})(Ti_{1"x}Zr_x)O_3$, where V represents vacancies in the crystalline structure.

Parameters Δ and ξ are similar in the Ln-doped BZT compounds to those obtained for Ln-free BZT. Compositional fluctuation is caused by oxygen vacancies that are generated by evaporation of TiO_2 and ZrO_2 in the sintering process (intrinsic vacancies) in Ln-free BZT. So, it can be concluded that the charge compensation mechanism not affect significantly the chemical disorder of BZT ceramics by addition of Ln^{3+} in the crystalline lattice for 5% of Ba^{2+} substitution.

TABLE 3. PARAMETERS $E'_{M,}$ T_M, Δ Y Ξ , DETERMINED BY SANTOS-EIRAS PHENOMENOLOGICAL MODEL FOR BT AND BZT CERAMICS AND LN-DOPED BZT CERAMIC WIT LN = GD, LA AND PR

Sample	ε_m	T_m (°C)	Δ (°C)	ζ
BT	512 4±10	132±0,1	21,46± 0,26	1,11± 0,01
BZT	286 2,66±12	107,3±0,1	40,96±0,37	1,61±0,02
BGZT	483 7,45±8	58,0±0,1	40,22±0,19	1,54±0,01
BLZT	665 9,49±19	7,0±0,1	38,46±0,25	1,76±0,01
BPZT	119 19,18±54	15,5±0,2	36,18±0,33	1,80±0,02

The LFD is usually associated with conductive processes of ions and electrons in materials (ceramics). The relaxation method is a way to characterize the conductivity processes in polycrystalline materials /20, 22-24/. Generally, electric modulus method ($M^* = 1/\varepsilon^*$) is employed to avoid the electrodes contribution to dielectric response in ceramic materials /25/.

In order to analyze the influence of the Zr^{4+} cation and the type of rare-earth cation on the conductivity process in the BT ceramic, we measured the dielectric response in $BaZr_{0.09}Ti_{0.91}O_3$, $Ba_{0.95}Gd_{0.033}Zr_{0.09}Ti_{0.91}O_3$, $Ba_{0.95}La_{0.033}Zr_{0.09}Ti_{0.91}O_3$, $Ba_{0.95}Pr_{0.033}Zr_{0.09}Ti_{0.91}O_3$ ceramics.

Figure 5 shows the frequency dependence of the imaginary part of dielectric modulus (M'') at different temperatures for BZT and, as an example, BPZT ceramics. It notes that the maximum value of the imaginary modulus increases and shifts to higher frequency values †with increasing temperature. This latter effect is a typical characteristic of a relaxation process.

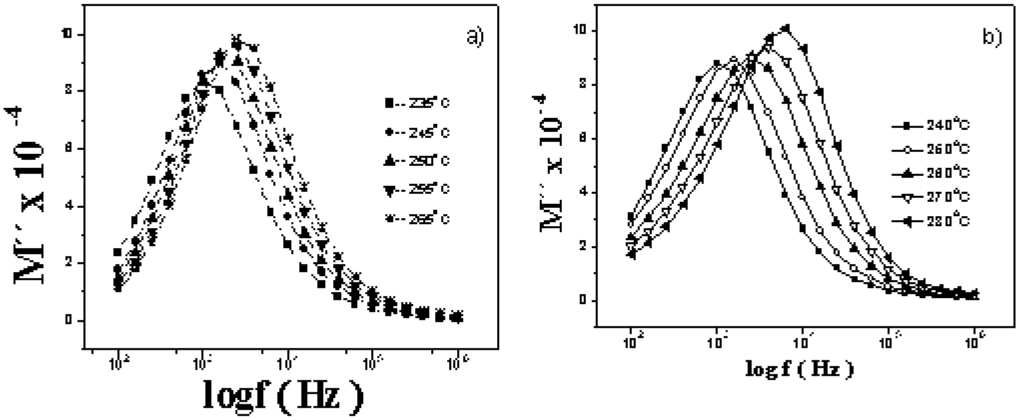

Fig. 5 Frequency dependence of the imaginary component of the dielectric modulus at different temperatures for the BZT and BPZT ceramics.

An relaxation distribution function of type Cole-Cole, $F^*(\omega) = \frac{1}{1+(i\omega\tau)^{\alpha}}$, is the best fit for the Ln-free BZT and Gd- and La-doped BZT samples. This function is characterized by parameter relaxation time, τ, and empirical parameter α, which takes a value between 0 and 1. For Pr-doped BZT sample, the function of best fit corresponded to a Havriliak Negami distribution function, $F^*(\omega) = \frac{1}{\left[1+(j\omega\tau)^{1-\alpha_{HN}}\right]^{\beta_{HN}}}$, which is characterized by τ, α and βHN parameters.

Figure 6 shows the temperature dependence of τ for each doping. The relaxation time exponentially decreases with increase of the temperature, and meets with the Arrhenius relationship for all samples. The activation energy, Ea, obtained through the line slope for the dependence of ln τ against the inverse absolute temperature (1 / T), is shown in figure 7.

Comparison of the values of Ea in the BT (0,71 eV) /20/ and BZT (0,81 eV) ceramics is up to the conclusion that the mechanism that causes the conductivity process in both materials is similar. Therefore, the conductivity in the BZT ceramic is associated with the movement of the singly ionised oxygen vacancies, which are generated by the loss of TiO_2.

The substitution of Ti^{4+} by Zr^{4+} only lowering the temperature at which begins the dielectric anomaly (about 200 °C). This is because the ZrO_2 has a melting temperature of the 115 0 °C, which is the 150 °C lower than the melting temperature of the TiO^2. So, oxygen vacancies appear in the process of obtaining the BZT ceramic at lower temperature.

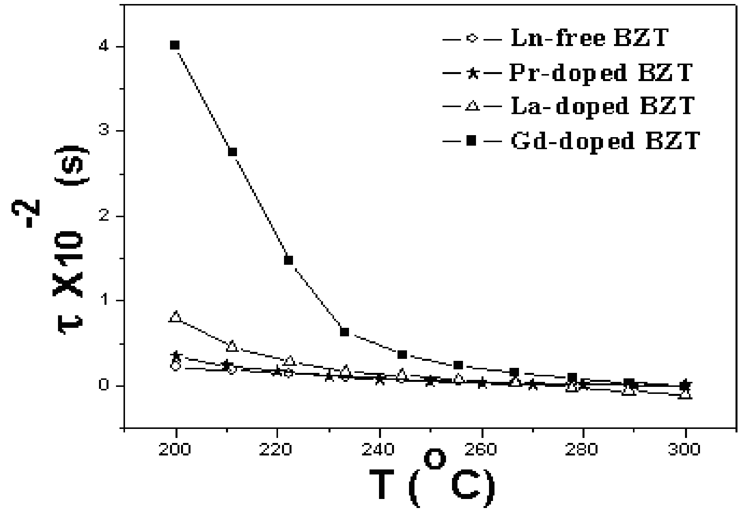

Fig. 6 Temperature dependence of the relaxation time for Ln-free, Gd-, Pr- and La- doped BZT ceramics.

The defect reaction equation is as follows:

$$O_{\circ}(lattice) = v_{\circ} + \frac{1}{2}O_2(g)$$

$$v_{\circ} = v_{\circ} + e'.$$

Where O$_{o}$ are the oxygen atoms, V_O oxygen vacancies and e' represents the electrons produced in the ionization process of the oxygen vacancies. Therefore, the movement of oxygen vacancies is a small contribution of conduction of electrons.

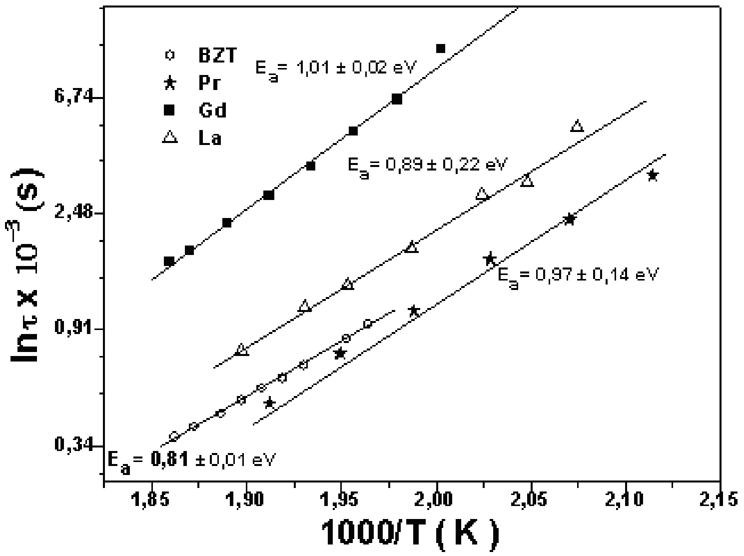

Fig. 7 Inverse of the absolute temperature dependence of the lnτ for BZT, BGZT, BLZT and BPZT ceramics.

The values of Ea for samples BGZT (1,01 ± 0,02 eV), BLZT (0,87 ± 0,14 eV) and BPZT (0,89 ± 0,22 eV) can be considered similar and higher than the values for BZT (0,81 ± 0,01 eV) ceramic. The activation energy increase can be explained considering that, in the charge compensation mechanism, the compensation mechanism by conduction of electrons is added when Ln^{3+} cations are introduced. The reaction equation is as follow for the La^{3+} cation:

$$La_2O_3 \rightleftharpoons 2La^{\cdot}_{Ba} + 2O_O + \tfrac{1}{2}O_2(g) + 2e'$$

Hence, it can be deduced the electronic contribution is higher because the number of electrons per unit volume is increased. This fact is evident in ε'_m values, which are higher than in BZT and may even be higher than in BT ceramics (see table III), suggesting that the donor contribution of this doping causes an increase in the permittivity. Furthermore, it should be influencing the ferro-paraelectric phase transition.

Conclusions

A diffuse phase transition is observed in the substitution isovalent of Zr^{4+} by Ti^{4+} into the BT ceramic for the composition of 9 % of the Zr^{4+} cation. When Gd^{3+}, La^{3+} and Pr^{3+} doped BZT ceramic for 5 % of Ba^{2+} substituted, no perceptible change in the diffusivity of the phase transition is verified. All the samples showed no relaxor behaviour.

The activation energy (0,81 eV) of conductivity process, observed in BZT ceramic, indicate the charge compensation mechanism seems to be singly ionised oxygen vacancies but with a small contribution of the movement of electrons.

The relaxation dynamics of conductivity process showed that for Gd^{3+}-, La^{3+}- and Pr^{3+}-doped BZT compound appears a strong contribution of the conduction of electrons mechanism due to the substitution the lanthanides ions onto Ba-sites.

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